DEVELOPMENT OF CHLORINE-RESISTANT AND NON-FOULING REVERSE-OSMOSIS MEMBRANES FOR WATER TREATMENT

Final Technical Report

to

U. S. ARMY BELVOIR RD&E CENTER

Project 7692

Southern Research Institute

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The three components in the production of potable water used by the reverse-osmosis water purification units (ROWPU) are pretreatment, membrane elements, and post-treatment. This project addresses only the first two components, which are the areas where improvements are most needed. In the pretreatment of feedwater, suspended, colloidal particles that can foul the membrane are removed by the use of flocculants/coagulants and scale inhibitors. Chlorine is also added to reduce microbial populations that can foul the membrane. Because the addition of chlorine in the feedwater causes membrane breakdown and reduces its useful life, an objective in the project was to develop a chlorine-resistant polymer for the RO-membrane. Another objective was to prepare and evaluate a more effective pretreatment polymer for removing foulants. In this project a novel, pretreatment polymer was designed, prepared, and found to be as effective as a flocculant during comparative evaluations against existing pretreatment polymers. However, there is still room for improvement because the compositions were not optimized. The novel polymer is a cationic polymer bearing crown-ether moieties for complexing with metal ions, which is designed to provide secondary mechanisms for flocculatio

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that might facilitate settling and filtration. A chlorine-resistant polymer for use in preparation of the RO-membrane was designed based upon selected functionalities that are known to have inertness towards chlorine. The novel RO-membrane polymer was difficult to realize, but a practical, synthetic route to the necessary monomer was developed. The monomer is water-soluble, which may indicate that water flux could be high in a membrane based on the targeted polymer that contains that monomer.

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DEVELOPMENT OF CHLORINE-RESISTANT AND NON-FOULING REVERSE-OSMOSIS MEMBRANES FOR WATER TREATMENT

I. SUMMARY

This is our Final Report on Project 7692 entitled, Development of Chlorine-Resistant and Non-Fouling Reverse-Osmosis Membranes for Water Treatment. It describes our activities for the contract period of July 1, 1992 to June 30, 1993. The overall objectives of the contract were to prepare and evaluate new flocculating/coagulating (F/C) agents and reverse-osmosis (RO) membrane polymers that may be used to improve the reverse-osmosis water purification units (ROWPU) currently fielded by the Army. The development of the two components were conducted in parallel.

We have had some success in synthesizing a prototype F/C polymer, the first component of the project. In this part of the project, we optimized not only the conditions for preparing the necessary monomer, but also the conditions for polymerizations. Cursory comparative evaluations of the first prototype indicated that the polymer can indeed function as a flocculating/coagulating agent. Because of the various difficulties that we encountered early on, we have not been able to prepare a series of polymers for a more comprehensive evaluation to further optimize the F/C polymer based on its performance attributes. We believe we have overcome the major difficulties in the synthesis of the monomer for the F/C polymer.

In the development of the RO-membrane polymer, our efforts were usually successful when performing the initial steps of the synthetic routes. Often we ran into difficulties when performing successive steps, which led us to continually modify the synthetic routes. In those synthetic routes in which we were able to carry out all the steps, the yields of the desired monomer were low. This is not entirely discouraging because it confirms that the desired monomer is a stable molecule. Furthermore, this area of the project ended on an optimistic note because we successfully synthesized an alternate monomer using a reaction scheme that affords practical yields. Given the opportunity to further pursue the polymer, preparation of the polymer is still a realistic goal.

The following sections detail our research accomplishments in each of the two areas of the project.

II. RESEARCH ACCOMPLISHMENTS

A. Development of F/C materials

1. Introduction

The FC materials under development will ultimately be used as a pretreatment polymer for removing foulants from water. Currently, the only existing synthetic cationic quaternary ammonium polyelectrolyte approved by USPHS for use in potable water clarification is the homopolymer of diallyldimethyl ammonium chloride (DADMAC). This polymer was originally prepared by Butler in 1951.[1] We rationalized that a structural modification of the DADMAC polymer, through a copolymerization scheme, will lead to a polymer that contains functionalities for specifically binding with metal ions. Because most RO-membrane elements are used for purifying water from natural sources, most of the foulants are humates that are anionic in nature. At the pH of water, the anionic materials can be expected to be associated with naturally abundant metal cations forming a shell of positive charge that leads to electrostatic repulsion, which, in turn, prevents the particles from aggregating and settling.

It is our hypothesis that by having metal ion-complexing groups in the FC polymer, an additional mechanism for flocculation can take effect, which may increase the rate and volume of colloidal accumulation in the feed water to the RO-membrane thereby facilitating their removal by filtration and increasing the service life, capacity, and efficiency of the RO-membrane.

A model chemical functionality that we chose to serve as a metal ion-complexing group is a crown ether. For this project, we chose a size for the crown-ether moiety that could complex specifically with sodium and potassium. The structure of the target polymer is similar to the USPHS-approved polymer except that our target polymer includes a monomer that contains the crown-ether moiety.

2. Synthesis of monomer for F/C polymer

The crown-ether-bearing monomer that we originally targeted for copolymerization was diallylmethyl-(2-[1-aza-18-crown-6])ethyl ammonium chloride (DAMACEAC), Compound 1A, the structure and synthetic route of which are shown in Figure 1. The first step of that route was the reaction of the diallylmethylamine with excess 1,2-dibromoethane to afford 2-bromoethylmethyldiallylammonium bromide (Compound 2A). The synthesis involved refluxing a 3:1 mole ratio of 1,2-dibromoethane and diallylmethylamine in dimethoxyethane. The reaction was straightforward and afforded a yield in excess of 80%.

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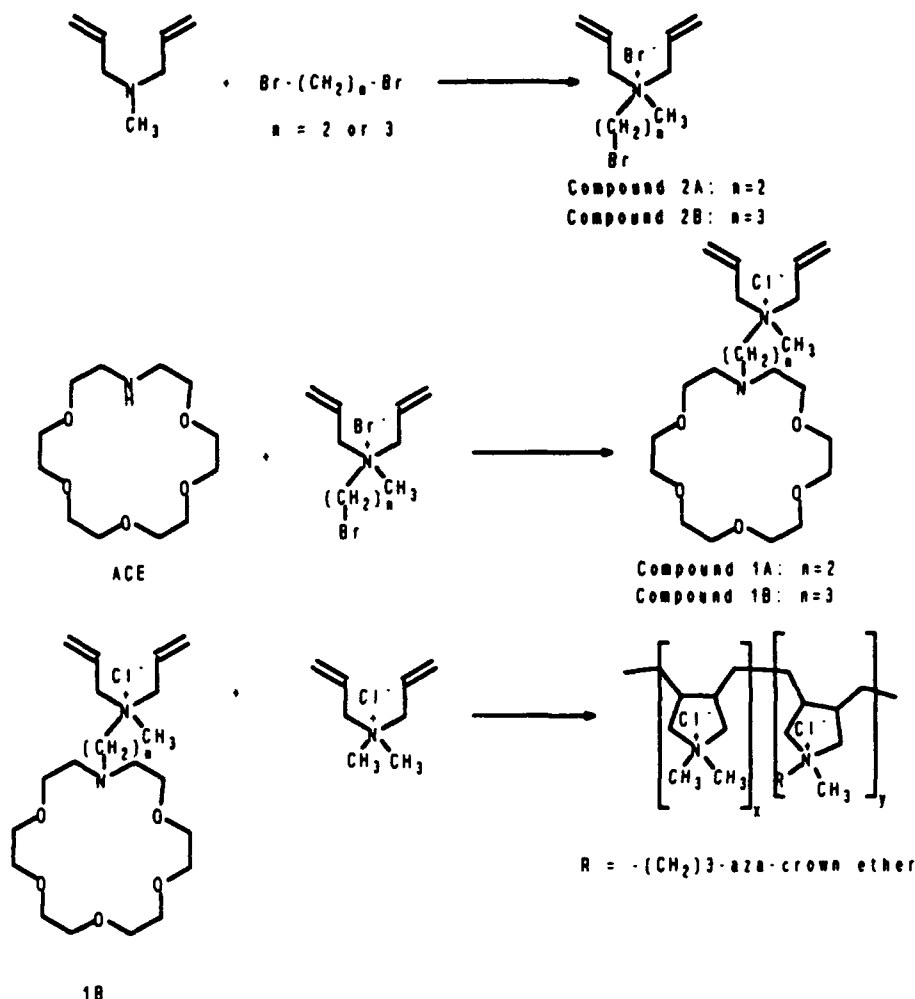
Figure 1. Synthetic route to flocculant/coagulant polymers.

The second step of the synthesis was not as straighforward as the first. All of our attempts to react Compound 1A with 1-aza-18-crown-6, as described in the monthly reports, resulted in a product mixture that was difficult to purify. Because the target compound and starting materials have similar solubilities, purification by recrystallization was difficult. Because the starting and target compounds are also salts, they were difficult to purify by distillation. Although the thin-layer chromatography (TLC) of the product mixture on alumina TLC plates using 9:1 (v/v) chloroform/ acetone solvent system, showed that the components may be separable by column chromatography, the relative amounts of the components did not look favorable for obtaining good yields, even after chromatography; thus, the reaction was not proceeding to completion. Therefore we attributed the low conversion to steric hindrance, which led us to lengthen the chain that separated the diallylamino group from the aza-

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crown-ether moiety in the target monomer. This eased the steric crowding at the center of substitution.

The subsequent target monomer for the F/C polymer became diallylmethyl-(2-[1-aza-18-crown-6])propyl ammonium chloride (DAMACPAC), Compound 1B, structure and synthesis of which are also shown in Figure 1. Before we began to prepare Compound 1B, we required more 1-aza-18-crown-6, which we decided to synthesize as shown in Figure 2 below because it was expensive at $54.50/g. However, we
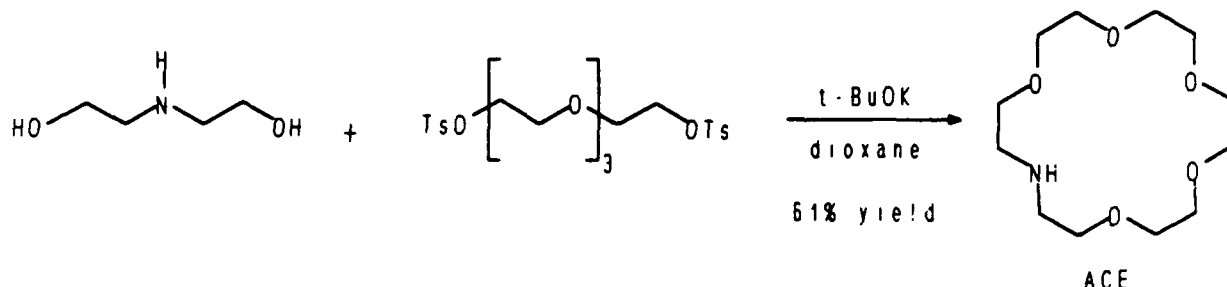

Figure 2. Reported synthesis of 1-aza-18-crown-6.[2]

soon realized that the literature procedure we were following was not as straightforward as described.[2] We ran into difficulty duplicating the synthesis but were able to obtain some 1-aza-18-crown-6 for our use, although at a lower yield than expected. The main difficulty with the synthesis was the purification. The template potassium cation used in the synthesis was complexed with the crown-ether with tosylate as the counterion. This was also a good indication that the target F/C polymer may have complexing capability if it contains the aza-crown-ether moiety. We eventually modified the work-up procedure in the synthesis of 1-aza-18-crown-6 by acidifying the compound so that it was not complexed with potassium. This modification allowed us to obtain the compound in yields comparable to those reported in the literature. We also continued to purchase the compound as needed because of time constraints.

Referring to the synthesis of Compound 2B shown in Figure 1, the reaction was just as straightforward as the synthesis of Compound 2A; however, there were some impurities that we did not previously notice in the synthesis of Compound 2A. One of these impurities was the product from the substitution of both bromides in the 1,3-dibromopropane to give a bis-quaternized compound. While this was a negative result, it was positive information in that it confirmed our hypothesis that the bromide in Compound 2A was too sterically hindered for substitution when it was subsequently

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reacted with 1-aza-18-crown-6. Hence, substitution of both bromides of 1,2-dibromo-ethane by diallylmethylamine did not readily occur.

Other impurities that were present with Compound 2B were eventually eliminated when synthesis was repeated using predistilled 1,3-dibromopropane and diallylmethylamine. This afforded Compound 2B in good yields with the least amount of impurity. The remaining impurity, the bis-quaternized compound, was not expected to interfere in the next reaction, and this was confirmed in a small-scale reaction of the crude 3-bromopropyldiallylmethylammonium bromide with purified 1-aza-18-crown-6. This reaction was found to yield the desired product, but there were impurities that consisted mostly of the starting materials plus the carryover impurity of bis-quaternized compound. These impurities were all confirmed by mass spectrometry (MS). By-products resulting from dialkylation of the aza-crown-ether nitrogen were not found in the MS.

The presence of the starting materials indicated the reaction was not going to completion. Furthermore, the low resolution on TLC of the product relative to the starting materials, 1-aza-18-crown-6 and 3-bromopropyldiallylmethylammonium bromide, posed a purification challenge. It became apparent at this point that an optimization of the reaction was necessary.

One variation of the reaction that can be used to reduce the presence of one of the starting materials is to use an excess of the other material. In this case, we had a choice of using either an excess of 1-aza-18-crown-6 or of 3-bromopropyldi-allylmethylammonium bromide. We weighed the consequences of each choice and opted to use an excess of the 1-aza-18-crown-6. This way, the potential quaterniza-tion of the 1-aza-18-crown-6 by dialkylation was avoided, which alleviated some of the purification problems. However, removal of the unreacted 1-aza-18-crown-6 from the product still needed to be addressed.

Use of excess 1-aza-18-crown-6 also increased the amount of impurities from the pre-existing impurities in the 1-aza-18-crown-6. These impurities were not identified and could not be removed from the 1-aza-18-crown-6 despite repeated recrystallizations before using. Fortunately, these unidentified impurities resolved cleanly from the desired product on the TLC. This paved the way for using column chromatography for purifying the monomer.

Therefore, we repeated the reaction of 1-aza-18-crown-6 with 3-bromo-propyldiallylmethylammonium bromide on a realtively larger scale to prepare the desired monomer for the polymerization studies. The TLC of the isolated product indicated the presence of the desired monomer with traces of four other compounds. The two major impurities were the bis-quaternized impurity described earlier and unreacted 1-aza-18-crown-6. Of these two impurities, the bis-quaternized impurity is the most undesirable because it can act as a crosslinking agent during copolymeriza-

tion of the aza-crown-ether monomer with diallyldimethylammonium chloride. The minor impurities were the impurities that were originally present with the 1-aza-18-crown-6.

Purification of the aza-crown-ether monomer required an extensive amount of time to develop. The TLC was a good indicator that column chromatography was the method of choice for separating the aza-crown-ether monomer from the bis-quaternized impurity; however, the separation of the 1-aza-18-crown-6 from the desired compound was questionable because the two compounds were barely separable on TLC.

The column that was used for purifying the aza-crown-ether monomer was packed with neutral alumina and eluted with a 9:1 ratio, by volume, mixture of chloroform and acetone. The trace impurities eluted first, followed in order by the 1-aza-18-crown-6 and the aza-crown-ether monomer. The bis-quaternized compound basically remained at the origin of the column but was stripped from the column by changing the eluting solvent to methanol. As thought, the column was not very efficient in resolving 1-aza-18-crown-6 from the monomer and one of the other trace impurities. Thus, a second purification technique was employed.

Because the 1-aza-18-crown-6 was recrystallized from hexanes, and the desired compound contained a quaternized functionality and therefore was water-soluble, the method of choice for the second purification was a liquid-liquid extraction using a continuous extractor. The product mixture that was recovered from the column chromatography was dissolved in water and placed in the continuous extractor. Hexane was refluxed to continuously extract the aza-crown-ether and the trace impurit· from the desired compound. After two weeks of continued reflux, this extraction did not completely remove the impurity, although it did reduce the amount of impurity.

We further reduced the amount of impurity by extracting the aqueous phase with methylene chloride, however, this extraction also removed some of the desired compound. As a result of this, we did not attempt to fully extract the impurity by this method in an effort to maximize yields. The aqueous solution was then evaporated to dryness to afford 4.9 g of the purer monomer. Because the extraction process proceeded too slowly, we decided to recover the monomer together with its impurity for the polymerization. It was not anticipated that the aza-crown-ether impurity would interfere with the polymerization since the monomer contained an identical aza-crown-ether functionality. It was anticipated that the low-molecular-weight impurity could easily be extracted from the polymer in the purification.

In a subsequent scale-up, we investigated the potential benefit of reversing the order of the chromatographic and extraction steps. This led to further improvements in the monomer synthesis because the extraction step was more efficient in

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removing impurities than column chromatography, which eliminated the labor-intensive chromatographic step. Also, we changed the extraction solvent from hexanes to methylene chloride. The excess 1-aza-8-crown-6 was more soluble at ambient temperatures in methylene chloride than in the hexanes previously used for purification of the aza-crown-ether by recrystallization: Thus, the synthetic route became more practical.

An alternative route that has the same number of steps to the aza-crown ether monomer, is shown in Figure 3. This was investigated as a potential backup in case of difficulty with the first route. We found that the alkylation of 1-aza-18-crown-6

Compound 3

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Compound 4
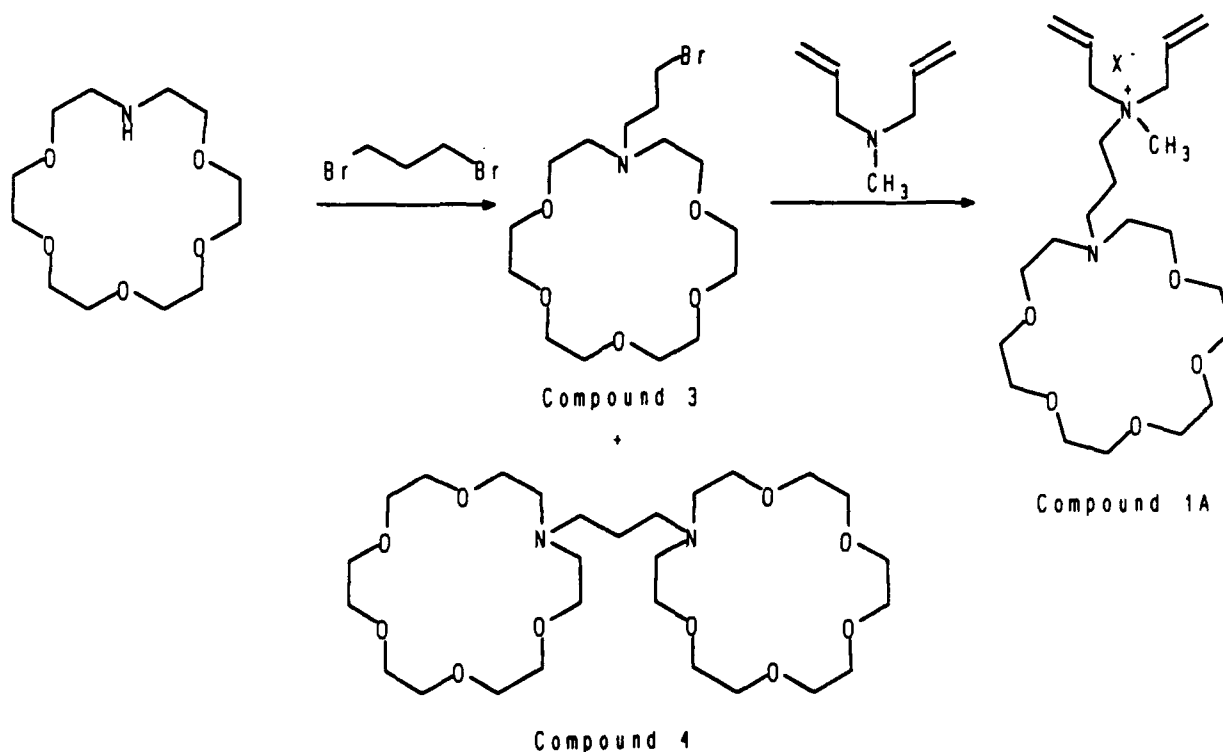
Compound 1A

Figure 3. Alternate route to new aza-crown-ether flocculant/coagulant material.

with the 1,3-dibromopropane afforded the desired compound, N-(3-bromopropyl)-1-aza-18-crown-6, with 1,3-bis(1-aza-18-crown-6)propane as a side product. The isolation of these two products indicated the absence of steric hindrance at the other substitution site, and the nitrogen of the aza-crown-ether does not become quaternized. This route has not been pursued further because the other route afforded better yields.

We also attempted to determine the feasibility of using the alternate approach shown in Figure 4. The first step in the approach is the conversion of the diallyl-

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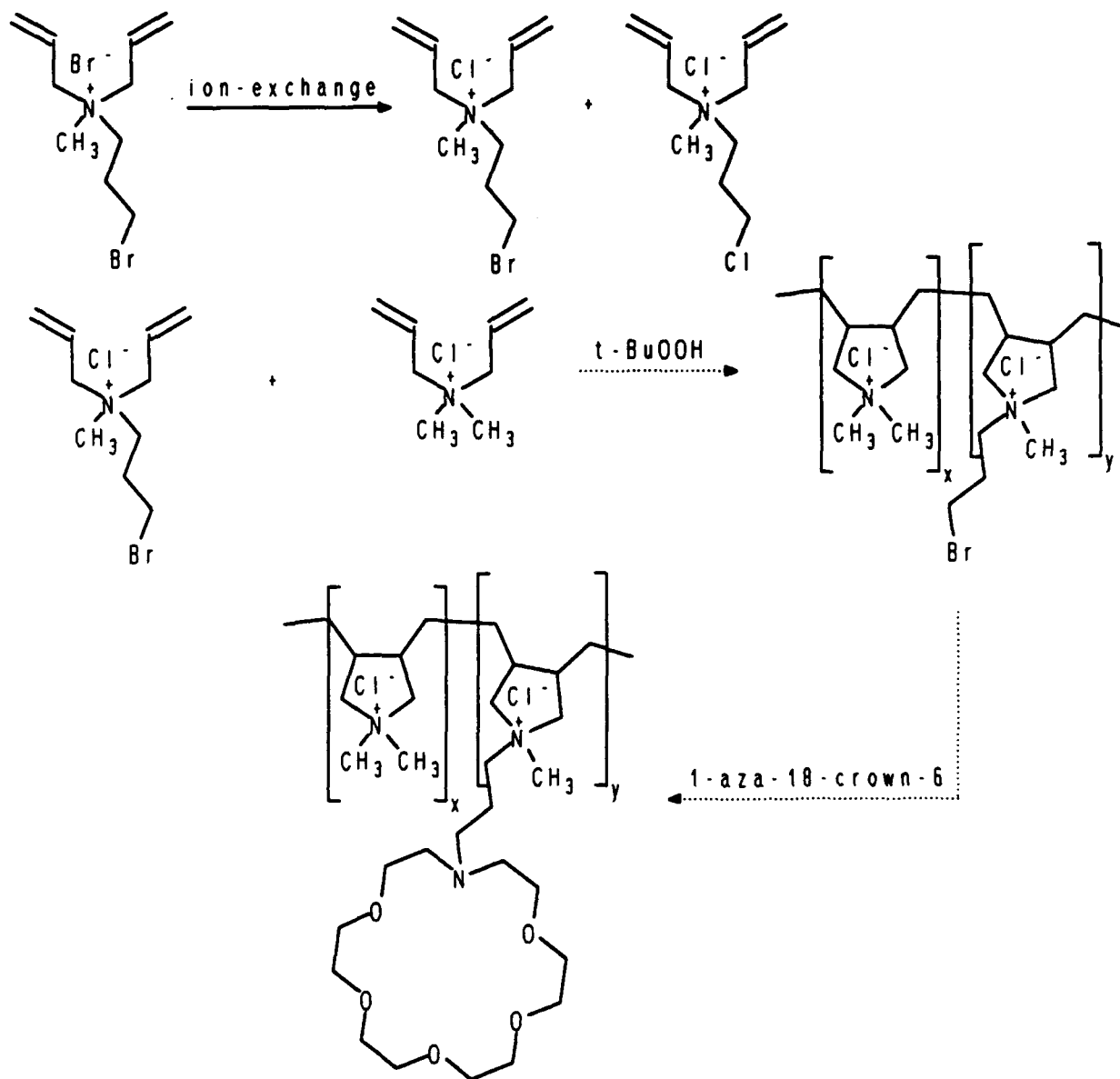
Figure 4. Alternate route to flocculant/coagulant polymer.

methylbromopropyl ammonium bromide into the corresponding ammonium chloride salt by ion-exchange. The conversion is necessary because the chloride salts of diallyldialkyl quaternaries polymerize more readily than the bromide salts. During the attempted conversion, an undesirable halide exchange side reaction was encountered, which resulted from the partial conversion of some of the bromopropyl groups into chloropropyl. Because of this side reaction, it may be desirable to prepare diallylmethylchloropropyl ammonium chloride as the preferred comonomer. However,

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we did not pursue this approach further because of our preliminary success in the copolymerization of the aza-crown-ether-bearing monomer.

3.   Polymerization studies

   a.   Homopolymerization of diallyldimethylammonium
         chloride (DADMAC)

   One of the controls for evaluation of the FC material was a polyquat polymer of diallyldimethylammonium chloride. This polymer was prepared according to two published procedures.[1,3] In the procedure of Butler et al., t-butylhydroperoxide was the initiator, while Boothe et al. used ammonium persulfate. In our first attempt, we used the Boothe procedure because it was readily adapted for copolymerizations, while Butler's procedure was only a homopolymerization. When our initial copolymerization attempt failed to produce a polymer, we resorted to Butler's procedure.

   The polymer prepared using Boothe's procedure had an inherent viscosity of 0.64 dL/g which was measured in 1 N NaCl using a Cannon-Fenske viscometer. No other viscometric measurements were performed on this polymer because the procedure failed to yield a polymer in the copolymerizations.

   The polymer from the Butler procedure had an inherent viscosity in the range of 0.39-0.44 dL/g at various concentrations in 1 N NaCl using a Ubbelohde viscometer. From the raw data, reduced viscosities were also calculated. When the inherent viscosity and reduced viscosity were plotted together as a function of polymer solution concentration, an intrinsic viscosity for the polymer, which was 0.35 dL/g, was determined.

   b.   Copolymerization of aza-crown-ether monomer
         with DADMAC

   In our first copolymerization attempt, the aza-crown-ether monomer that we prepared for this polymerization still contained a small amount of 1-aza-18-crown-6 as impurity. However, because this impurity has some structural similarity to the monomer, we did not expect it to interfere with the reaction. Otherwise, the aza-crown-ether moiety of the monomer would also interfere during polymerization.

   Therefore, we proceeded to copolymerize the aza-crown-ether monomer (Compound 1B) with diallyldimethylammonium chloride, as shown in the third equation in Figure 1. In this first attempt, we set the comonomer ratio at 1:1 and adapted the procedure of Boothe as follows. The aza-crown-ether monomer and the diallyldimethylammonium chloride, which is commercially available as a 60% solution in water, were mixed together at the prescribed ratio. A small amount of EDTA was also added. The pH was then adjusted to 3 with dilute HCl, and a dilute solution of

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potassium persulfate was added. The reaction was allowed to proceed for three days before the reaction was worked-up. Based on visual observation of the consistency of the reaction mixture, the lack of discernable increase in viscosity indicated that the polymerization did not occur or the molecular weight was not very high. The work-up involved adding acetone to precipitate the polymer and extract the more soluble low-molecular-weight impurities. The syrupy precipitate was then isolated by decanting the solvent mixture and drying.

The characterization of the syrupy precipitate by NMR spectroscopy showed that it was essentially all aza-crown-ether monomer and that neither the polymer nor the DADMAC monomer were present. On closer inspection of the literature, we found that the polymerizations of the diallyldimethylammonium halides afford higher-molecular-weights when the halide is a chloride.[4] Therefore, we ion-exchanged the bromide of the aza-crown-ether monomer with a chloride. Also, on subsequent polymerization attempts we used Butler's procedure as well.

We also analyzed the aza-crown-ether monomer that we recovered by mass spectrometry (MS) to determine which halide ions were present. Although we previously treated the monomer with HCl before the polymerization, we were not certain if the procedure had adequately exchanged all the bromides. The MS did confirm the presence of both chloride and bromides. Thus, because some of the aza-crown-ether-monomer molecules were still as a bromide salt when we copolymerized it, this may have contributed to the lack of reaction.

We then converted the aza-crown-ether monomer from a bromide to a chloride salt by eluting an aqueous solution of the monomer through a column containing a chloride exchange resin. After evaporating to dryness, the monomer was recovered and analyzed by MS to confirm the completeness of the exchange.

Another polymerization was then attempted using the chloride salt of the aza-crown-ether monomer. We maintained the 1:1 comonomer feed ratio, but we used t-butylhydroperoxide as initiator instead of the ammonium persulfate that was previously used. Because the aza-crown-ether monomer contains an amine functionality, and peroxide initiators usually require amines as promoters, t-butyl hydroperoxide was considered to be a better initiator than ammonium perfsulfate. A concentration of 2 mol-% of the initiator was used based on the overall mole content of both monomers. The reaction was carried out at 65-70 °C overnight and worked-up by adding acetone to precipitate the polymer. The product from this reaction was solid, which led us to believe that the polymerization worked. Characterization by NMR spectroscopy indicated that it consisted mostly of unreacted ACE monomer and traces of polymer. Apparently, the presence of a small amount of polymer contributed to solidifying the ACE monomer, which was originally a highly viscous liquid. Therefore, we concluded that the ACE monomer was not readily incorporated into the polymer at the 1:1 comonomer feed ratio.

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We then used the recovered ACE monomer for another copolymerization attempt. In this copolymerization, the reaction conditions were similar to the previous ones, except that the ratio of the DADMAC to the ACE monomer was adjusted to approximately 9:1. The comonomer ratio was approximate because after recovery, the ACE monomer contained a small amount of impurity, which was primarily polymer of unknown comonomer ratio. Unlike the 1:1 copolymerization that became viscous, the 9:1 copolymerization reaction mixture solidified as it progressed. It was worked up by dissolving the mixture in water and precipitating the polymer with acetone.

Since the aqueous solution was highly viscous before the precipitation, we were certain that we had obtained a polymeric product. However, after precipitation, the spectral data from NMR spectroscopy indicated the presence of allylic hydrogens. These hydrogens were attributed to either residual monomers or unreacted allylic groups in the polymer. At that point, we were uncertain as to whether the polymer was impure or underwent polymerization through a different mechanism that left some allylic hydrogens intact.

Because it was easier to prove the presence of residual monomers, we purified the polymer for a second time by dissolving it in water and precipitating it with acetone. After drying the precipitated polymer, we recovered 4.75 g of the polymer and characterized it for a second time by NMR. The second characterization showed the absence of allylic hydrogens and confirmed the presence of both comonomers incorporated in the copolymer at the approximate feed ratio. We also evaporated the supernatant liquid from the precipitation and analyzed the residue by NMR. This residue contained a large concentration of allylic hydrogens. Additionally, we characterized a homopolymer of DADMAC by NMR, and it was found to have residual monomer. The NMR chemical shifts of the allylic hydrogens present in the poly(DADMAC) were identical to the allylic hydrogens present in the supernatant solution from the copolymer purification. This strongly suggests that all of the ACE monomer was either incorporated in the copolymer or completely removed in the first precipitation of the polymer. However, NMR data for the copolymer supported the conclusion that the ACE monomer was incorporated into the purified copolymer and was present at a level approximately equal to its concentration in the feed.

As the characterizations and evaluations on the initial model polymer indicated the potential utility of crown-ether-bearing polyquats as FC materials, additional polymers based on the same monomers at other comonomer ratios became synthetic targets for a comprehensive evaluation program aimed at optimizing the performance attributes. The DADMAC/DAMACPAC comonomer ratios targeted were 4:1, 7:3, and 3:2, with the lesser component being the aza-crown-ether monomer. Because of the ease that we previously experienced in preparing 9:1 copolymer, we thought the preparation of the series would be straightforward. This was not the case with any of the other three comonomer ratios.

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After copolymerization, all three comonomer feed ratios netted an insoluble polymer that swelled into a gel in water. Each copolymerization was similarly worked up by filtrating out the gel particles and concentrating the filtrate; however, most of the reaction products were gel particles, and the concentrated filtrate contained only low-molecular-weight materials. The gel particles were relatively fragile and were micro-nized after prolonged stirring of the suspensions. The suspensions became stable dispersions that did not fully settle, even after centrifugation. The dispersions also had some viscosity, which indicated that polymerization had occurred. Aliquots of these dispersions were placed in water at acidic and basic pH extremes and in 1N NaCl to determine whether the solubility of the copolymers were sensitive to pH or ionic strength. All of the copolymers did not dissolve in these solubility tests, and we concluded that polymerizations had occurred, but the polymers were crosslinked. Considering previous results, that the 1:1 comonomer ratio did not yield a polymer and the 9:1 ratio yielded a soluble, high polymer, we expected the results of the intermedi-ate comonomer ratios to be an intermediate of the two extremes. Thus, the results were unexpected. Time did not permit looking at solvent temperature or initiator effects on these copolymer products.

c.   F/C agent characterization and evaluation

The intrinsic viscosity of the 9:1 copolymer was measure in 1 N NaCl using a Ubbelohde viscometer as prescribed in ASTM Method D2857. Figure 5 shows the normalized plots of inherent and reduced viscosities as a function of concentration for the 9:1 copolymer. Ideally, the inherent and reduced viscosities have a common Y-intercept at zero concentration. The projected viscosity at zero concentration is the value reported for the intrinsic viscosity. That was determined to be 0.94 dL/g. Considering that the 9:1 copolymer was prepared using the same concentration of initiator as in the homopolymerization of DADMAC, the two polymers can be expected to have very similar molecular weights. The higher value obtained for the 9:1 copoly-mer was very encouraging.

Because the 9:1 copolymer has a functionality (aza-crown-ether) that can complex sodium ions, this complexation may contribute to an apparent increase in molecular weight that corresponds to the observed higher inherent viscosity. Because of the novelty of these crown-ether containing F/C polymers, it is not known how the presence of such a functionality can affect the solution properties of the polymer. Thus, caution should be exercised in comparing polymers having different composi-tions.

Another plausible explanation for the perceived discrepancy in molecular weights could be due to the differences in the mechanism of initiation. In both cases, the initiator was t-butylhydroperoxide. However, peroxides in the presence of amines
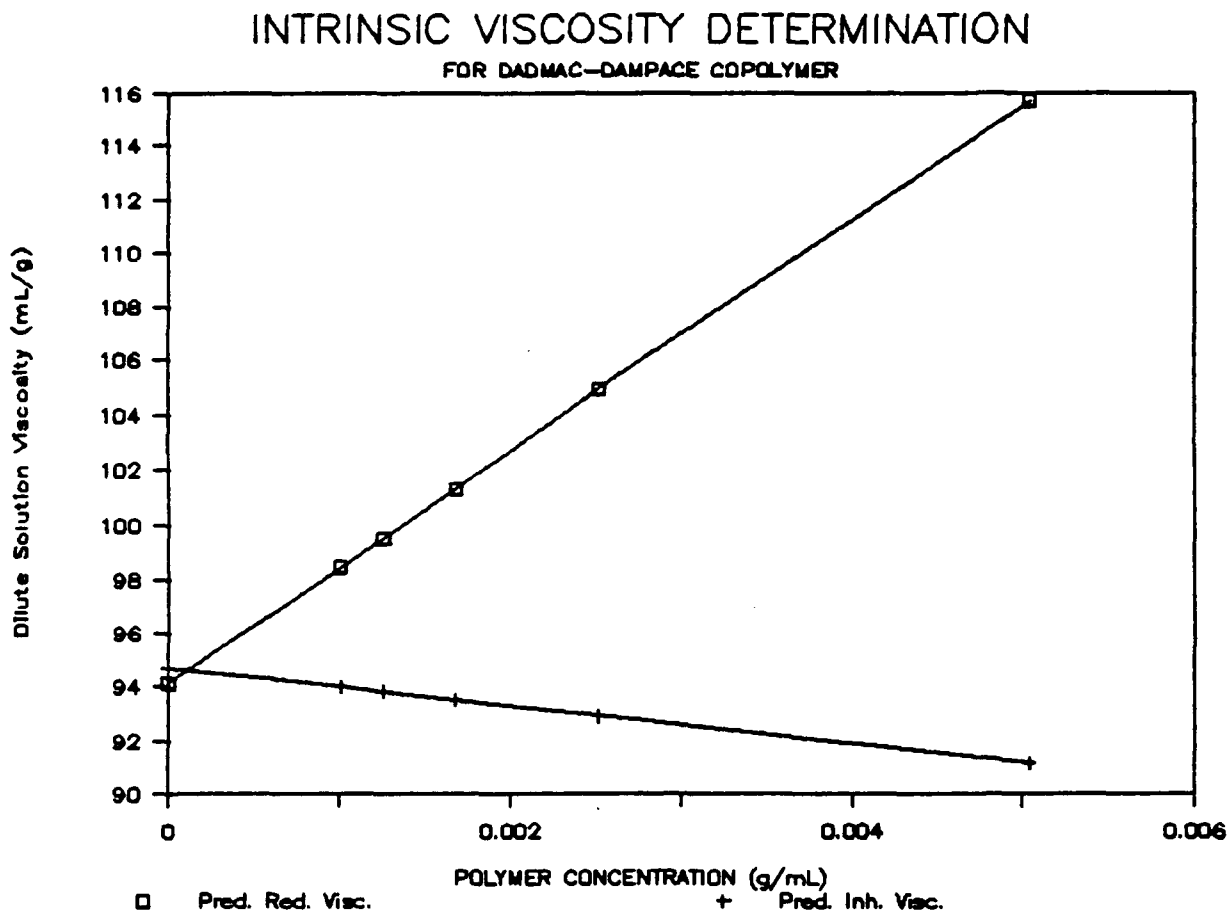
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INTRINSIC VISCOSITY DETERMINATION
FOR DADMAC—DAMPACE COPOLYMER

Figure 5. Determination of intrinsic viscosity of 9:1 copolymer.

are known to be stoichiometrically reduced to one free radical species per equivalent of amine, while thermal decomposition of a peroxide molecule produces two free radical species. In the case of the copolymerization, the presence of an amine functionality in the aza-crown-ether may have forced the mechanism of initiation to be a redox process. Thus, even if equal amounts of initiator were used, there would be twice as many free radical species available for the initiation of the polymerization of DADMAC than were available for the copolymerization with the aza-crown-ether monomer. Therefore, theoretically, the 9:1 copolymer should have twice the molecular weight of the DADMAC homopolymer.

In an effort to determine molecular weight, another attempted analysis was

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gel permeation chromatography (GPC). Without embarking on a major methods development program, we used the existing setup of our GPC instrumentation, which was set up for analyses using organic solvents, as the mobile phase and hydrophobic crosslinked polystyrene gels in the columns. The solvent was dimethyl acetamide containing 4 g $LiNO_3$/L of solvent. Unfortunately, this solvent could not dissolve the polymer, which precluded the analysis. A more probable solvent system for performing GPC would be in 1 N NaCl, the same solvent used in the viscosity measurements. This will require a hydrophilic column.

We have also attempted to evaluate the 9:1 F/C copolymer on a water sample taken from a local creek. The water was clear with only a small number of visible, suspended particles that appeared large enough to be filtered. The F/C copolymer was evaluated as a 0.2% aqueous solution. From a commercial 60% aqueous solution of poly(DADMAC), we also prepared a 0.2% solution for use as control. The evaluation was performed by dropwise addition of the diluted F/C polymer solution into a volume of the water sample. No flocculation or coagulation occurred in either case. We believe the water was too "clean" for this evaluation because it was sampled shortly after the melting of the winter snow in the Birmingham area. Thus, one of our objectives in the evaluation of the F/C polymer became the identification of a water source that will give a positive result when known F/C materials are added to it. This water source would then be used in all comparative evaluations of the F/C polymers.

We investigated the use of 0.2% aqueous solution of bovine serum albumin as a model for contaminated water because DADMAC polymers are known to be used in treating waste water from food processing plants. Our qualitative evaluations involved observations of flocculation in test-tube-size samples rather than conducting jar tests. We tested the 9:1 copolymer with the DADMAC homopolymer as control. Both of these polymers were tested as 0.2% aqueous solutions on the bovine serum albumin solution. In a series of six test tubes, one to six drops of a F/C-polymer solution was added. Flocs immediately formed in all of the test tubes but varied in the amount formed. We found that the 9:1 copolymer was more effective than the commercial poly(DADMAC) in flocculating the model of contaminated water. This observation was based upon the fact that there appeared to be more flocs in the 9:1 copolymer test tubes than in the poly(DADMAC) where the optimum dose seemed to have been exceeded. When the dose was exceeded, the amount of flocculation was observed to decrease.

We also tested the 7:3 copolymer to determine if it would exhibit F/C properties despite its lack of solubility. When a few drops of the 7:3 copolymer dispersion was added to a few mL 0.2% aqueous solution of bovine serum albumin, an increase in translucency of the dispersion was apparent. This was a good indication that the polymer may not necessarily have to be in solution to be functional.

We also requested and received a sample of Potomac River water from the

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U.S. Army Belvoir RD&E Center for evaluation. A cursory test on this water was attempted by adding a few drops of the 9:1 copolymer to a few mL of contaminated water. Flocculation seemed to have occurred since the turbid water acquired a faintly discernable cloudiness, which settled with time. Obviously, these "jar" tests would lead to more discernable results if the tests were done under ASTM specifications.

More work on these copolymers is needed. We continue to believe that these types of copolymer systems hold promise for improved F/C activity.

B.   Reverse-Osmosis Membrane Polymer Development

1.   Introduction

The RO-membrane under development was designed to be chlorine-resistant by assembling a molecular architecture of chemical functionalities that are known to be unreactive towards chlorine. The first step in the development of chlorine-resistant, RO-membrane began with monomer synthesis. Upon successful synthesis of the monomer, its polymerization was expected to lead to a polymer that could then be fabricated into RO-membrane films using conventional technology. Up to the end of the contract period, we have had a difficult time preparing monomer in the amounts required for polymerization; however, we continued to find promising alternate approaches. The following sections discuss the various approaches used to derive the monomer.

2.   Approaches to monomer for RO-membrane polymer

a.   Starting from 1,4-dicyanobenzene

The first route attempted in the synthesis of the RO-membrane monomer is shown in Figure 6. The first step of the synthetic scheme is the reaction of 1,4-dicyanobenzene with ethanol in the presence of hydrogen chloride to form a bis-iminoester (Compound 6). Three variations of this reaction were performed to obtain the product in high yield with good purity. The optimized procedure we developed involved dissolving the 1,4-dicyanobenzene in chloroform in the presence of the required amount of ethanol and bubbling HCl gas at 5-8 °C to obtain the corresponding iminoester hydrochloride, which formed as a precipitate and was recovered by filtration in nearly quantitative yield.

The next step of the synthesis is the transamination with glycine ethyl ester to prepare the diethyl benzene-,4-bis(ethoxymethylideneaminoacetate) (Compound 6). Despite adapting a literature procedure,[5] we have encountered an unexpected difficulty in this synthesis. Two attempts under different conditions gave identical negative results, which is the isolation of a mixture of compounds as indicated by TLC.
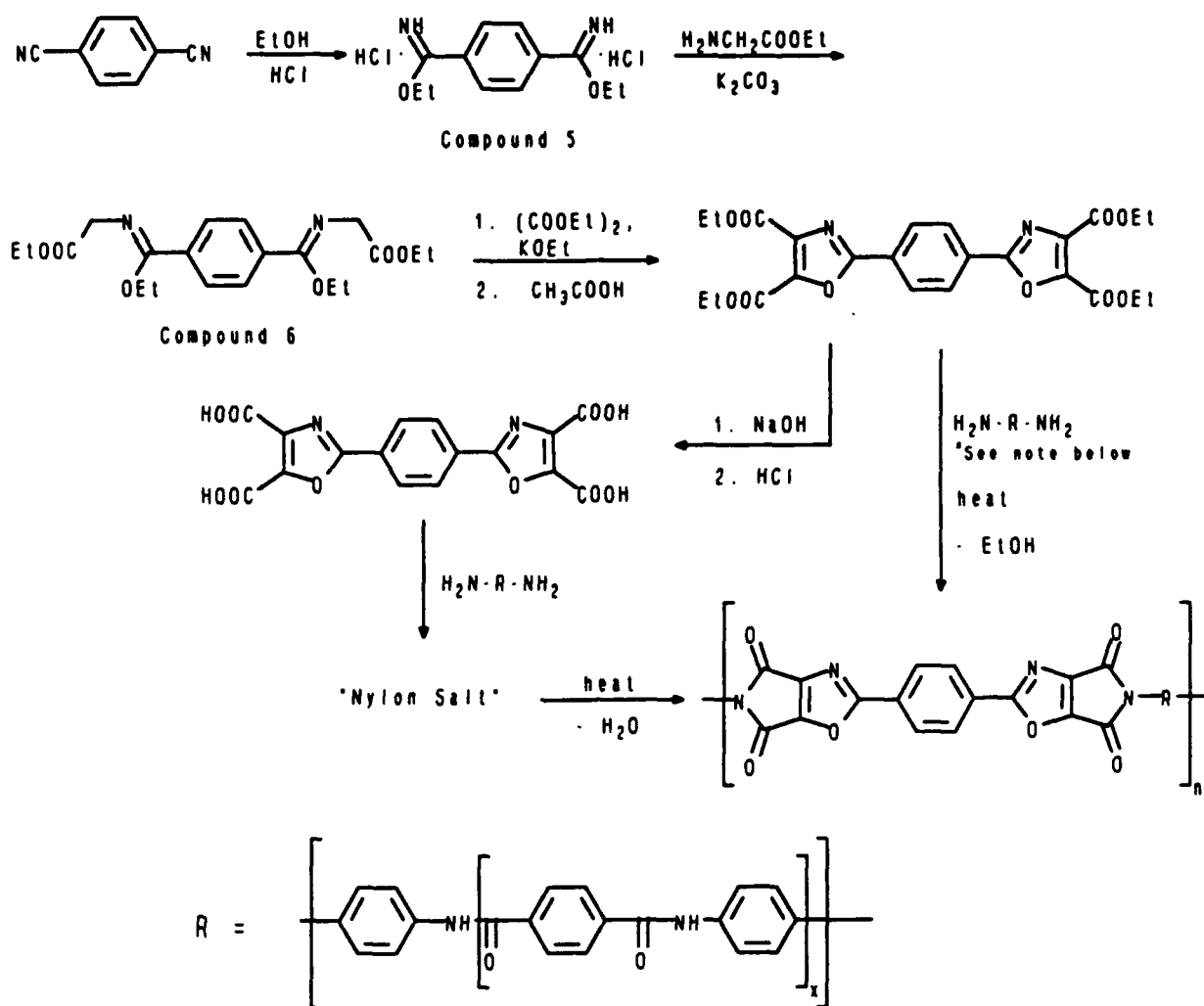
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Figure 6. Route to RO-membrane polymer via 1,54-dicyanobenzene.

Furthermore this mixture of products had a component that was unstable to air as indicated by its darkening. Purification by repeated recrystallization ultimately led to a low yield of pure product for spectrocopic analysis. This pure material was found to be the free base of Compound 5 and not the desired Compound 6. This result led us to hypothesize that Compound 6 may be an unstable compound. The decomposition process could be oxidative dehydrogenation, whereby the benzene ring becomes quinoidal so that conjugation is extended from one ester carbonyl to the other as shown in Figure 7 below.

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b. **Starting from terephthaloyl chloride**

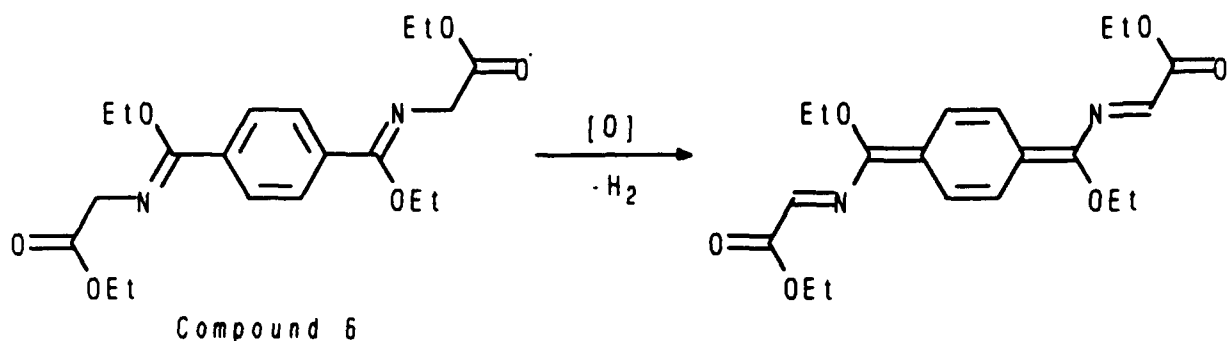Because of the unexpected result discussed above, we searched the literature

Figure 7. Hypothesized oxidative dehydrogenation of Compound 6.

for alternate procedures that could be adapted for preparing imidates such as Compound 6. A two-step synthetic route was found[6] that can be adapted to prepare Compound 6 as shown in Figure 8. This is the same number of steps as the previous route. The first step of the route is the reaction or terephthaloyl chloride with glycine ethyl ester to yield Compound 7. This was found to be straightforward and afforded
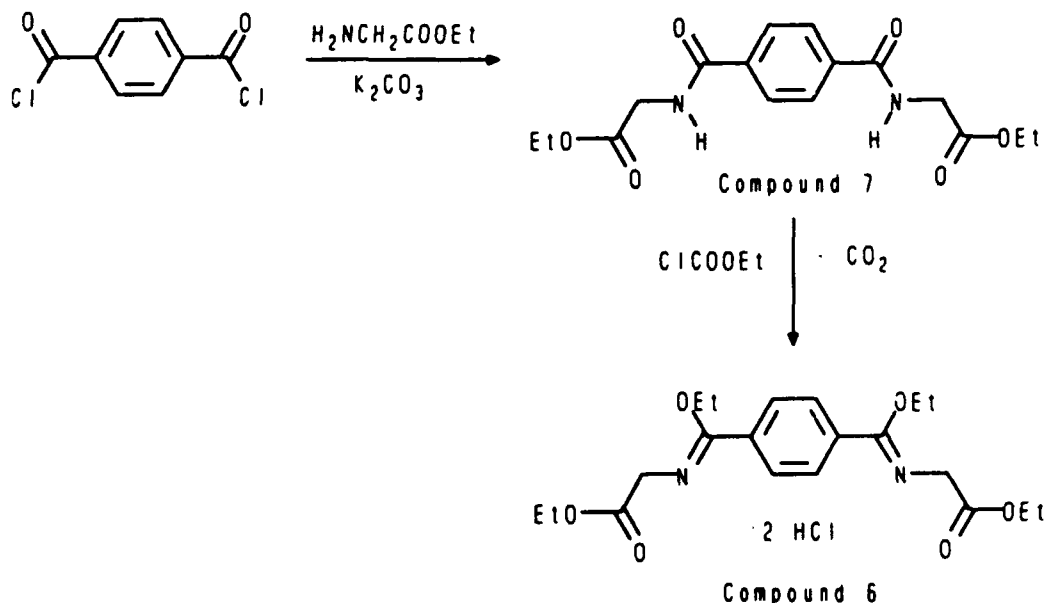

Figure 8. Alternate 2-step route to Compound 6.

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good yields. The second step, the one in which the terephthalamide derivative (Compound 7) is treated with ethylchloroformate, did not proceed as expected.

Difficulty in converting the terephthalamide derivative into the bis-iminoester derivative of bis-ethylglycineterephthalamide led us to conclude that electronic effects due to the substitution pattern on the benzene ring were responsible for the incomplete reaction.

c.   Starting from isophthaloyl chloride via amide
       or substituted amides

Because of the unexpected difficulty in converting the bis-ethylglycine-terephthalamide to its bis-iminoester derivative (Compounds 7 and 6, respectively, Figure 8), we changed the target compound to a structural isomer, which led to the use of isophthaloyl chloride instead of terephthaloyl chloride as starting material. This change was expected to circumvent the negative impact of electronic effects. The reaction steps were still identical to that shown in Figure 8. This new route is show in Figure 9 below.

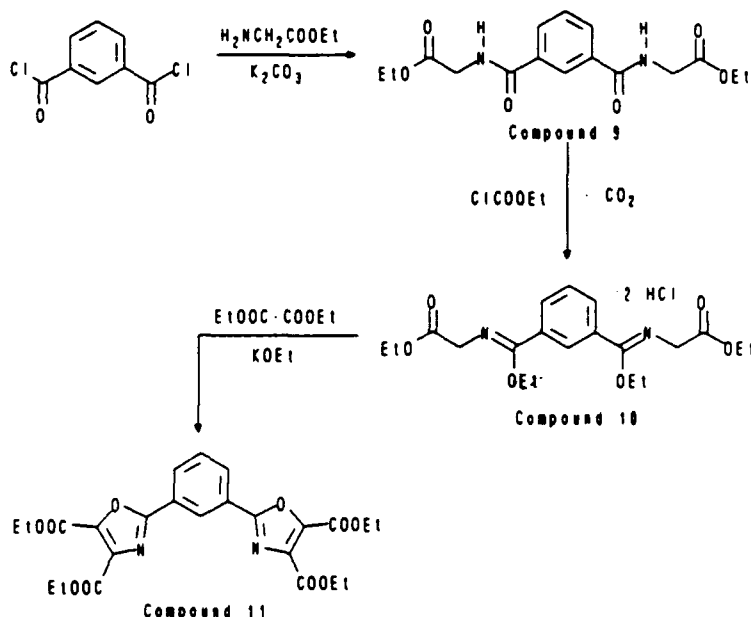The first step of the route was also straightforward. However, the next step in

Figure 9. Alternate route to monomer for RO-membrane polymer.

which bis-ethylglycineisophthalamide (Compound 9) was reacted with ethylchloroformate to obtain the bis-iminoester (Compound 10), did not proceed as expected. The mass spectrum of the product indicated the presence of a MW 392 compound, which

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should be the desired product (Compound 10). When we attempted to scale-up the reaction, we found that Compound 10 appeared to be moisture sensitive because it liquified upon exposure to air during the work-up of the reaction.

Because of this apparent moisture sensitivity, we attempted to by-pass the isolation of the derivative and directly react Compound 10 with diethyl oxalate in an effort to obtain the desired monomer (Compound 11). A low yield of a mixture of products, as evidenced by TLC, was isolated. The mixture was analyzed by MS and was found to contain a compound with a mass of 500 that supposedly belonged to the desired bis-oxazole functionalized Compound 11. Because of the unexpected result of moisture sensitivity and low yield, we looked further in the literature to find other practical methods of forming oxazoles, which are discussed in other sections below.

As parallel investigations of alternate routes to the monomer (Compound 11) proceeded, we searched for other methods of forming imino-esters. Although our previous results from an imino-ester route indicated to us that such compounds may be moisture sensitive, procedures found in the literature report the contrary. Thus, we devised and performed the route shown in Figure 10. In the route, Compound 9 was reacted with phosphorus oxychloride or phosphorus pentachloride. This reaction was an attempt to prepare a bis-iminochloride (Compound 13), which would have been reacted with ethanol to afford the bis-iminoester (Compound 10). Instead, the isolation of Compound 14 convinced us that ring-closure from an isophthalamide derivative would be the best approach to the monomer for the RO-membrane polymer. This negative result led us to the identification of a preferred approach. The routes for
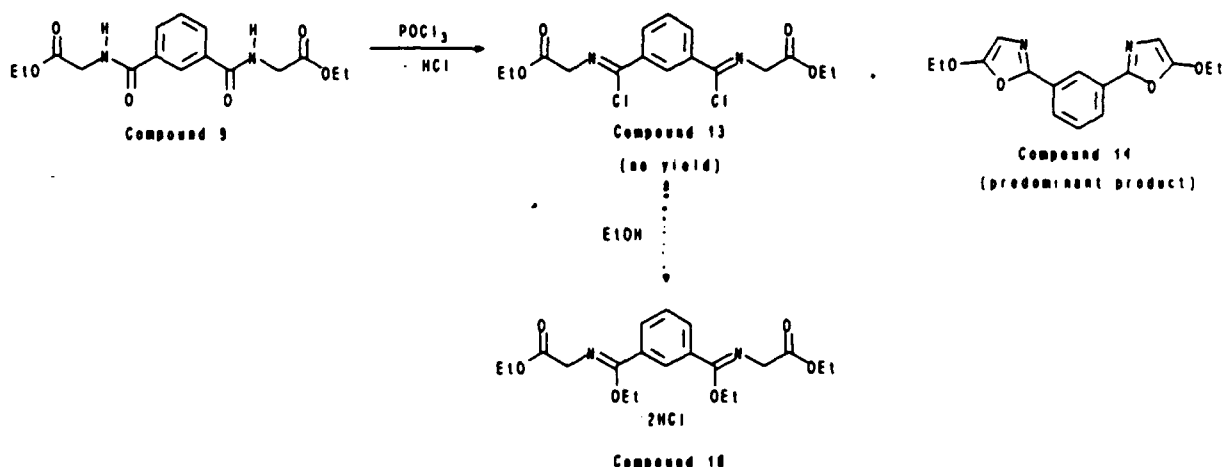

Figure 10. Reaction of bis-glycine isophthalamide with phosphorus oxychloride.

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preparing the appropriate isophthalamide derivative for the subsequent ring-closure with phosphorus oxychloride are discussed in subsequent sections.

Thus, the appropriate isophthalamide derivative would be Compound 16, which can be approached by the route shown in Figure 11. Using this route,
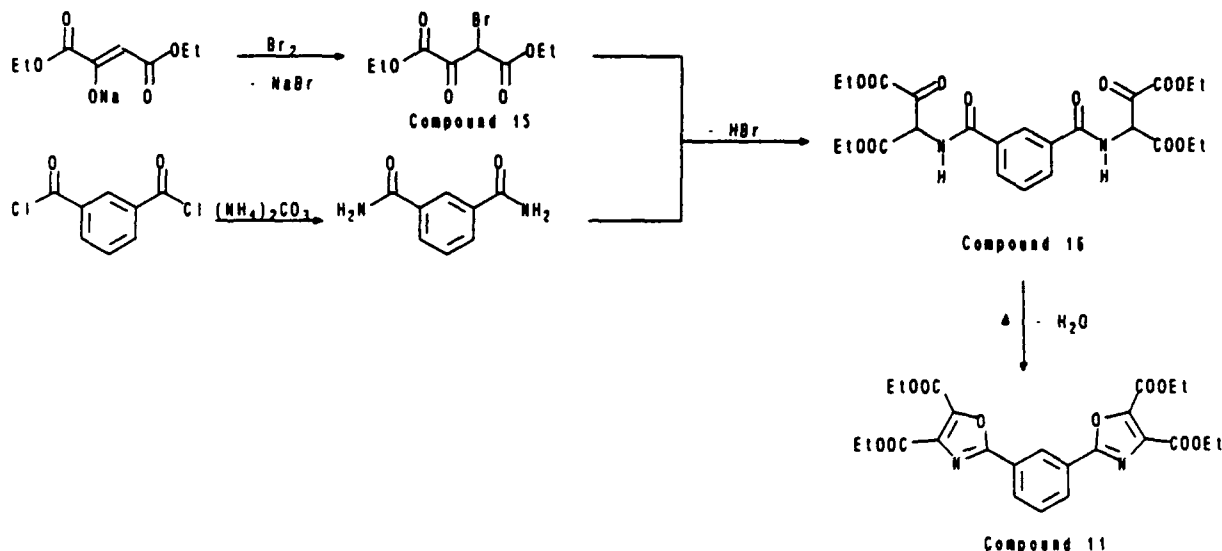

Figure 11. Attempted one-step synthesis of monomer for RO-membrane polymer.

isophthalamide was prepared from isophthaloyl chloride by reacting it with either concentrated ammonium hydroxide or ammonium carbonate. The isophthalamide was then alkylated with ethyl bromooxaloacetate (Compound 15), which was previously prepared according to a reported procedure.[7] The alkylation procedure was attempted under four different conditions in an effort to obtain Compound 16.

In the first attempt, a reported procedure was adapted, whereby the isophthalamide and Compound 15 were reacted together in bulk at 120 °C.[8] In this adapted procedure, isolation of Compound 16 was not necessary because it was expected to spontaneously dehydrate with ring closure under elevated temperatures for alkylation. The reaction mixture remained heterogeneous throughout the reaction time. After work-up, the isolated product was found to contain primarily the starting material isophthalamide. MS analysis indicated the absence of both potential intermediate and the desired product. The lack of reaction was probably a result of the lack of solubility of the isophthalamide in the ethyl bromooxaloacetate.

In a second variation of the alkylation, a published procedure was also adapted whereby the ethyl bromooxaloacetate was generated in situ in the presence of the isophthalamide.[9] Isophthalamide and sodium diethyl oxaloacetate were dissolved in N-methyl pyrrolidinone containing a stoichiometric amount of bromine relative to the amount of sodium diethyl oxaloacetate. After work-up, only isophthalamide was

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isolated. Further attempts to identify other reaction products led to the identification of an adduct of the N-methyl pyrrolidinone and the ethyl bromooxaloacetate as shown in Figure 12. Though this result was negative, it was a positive indicator that the bromide in ethyl bromooxaloacetate is very labile and should be easily displaced by weak and even bulky nucleophiles.
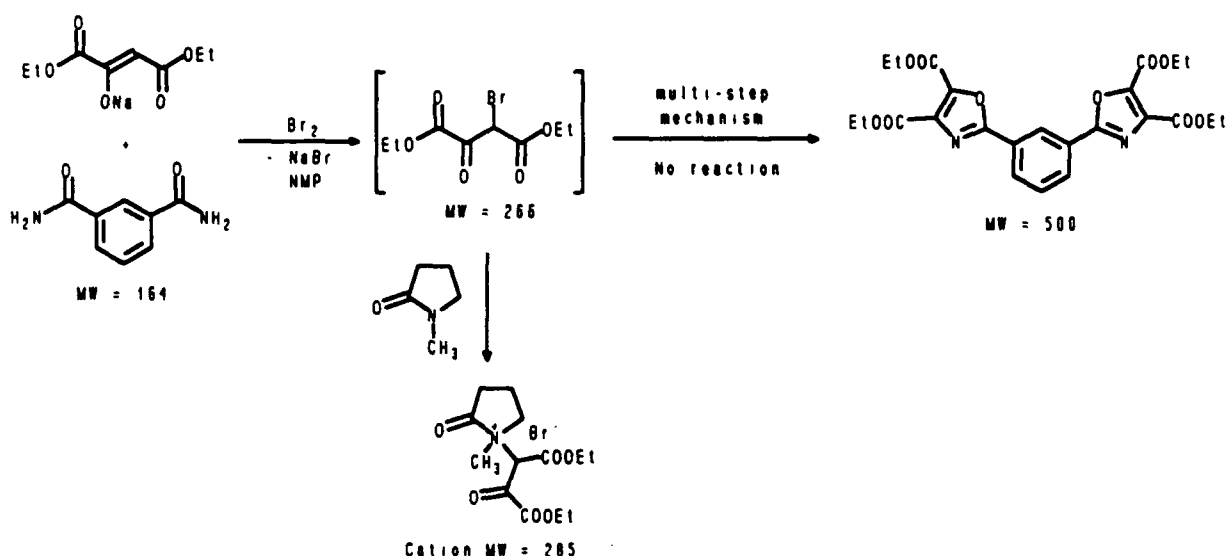

Figure 12. Synthesis of precursor to monomer for RO-membrane polymer.

The third unsuccessful attempt was aimed at first derivatizing the isophthalamide into a soluble derivative that could be alkylated. We reacted the isophthalamide with trimethylchlorosilane in an attempt to convert it into a soluble silylated derivative that could be reacted with the ethyl bromooxaloacetate. After refluxing the isophthalamide in the trimethylchlorosilane for several days, there were no visible signs that the reaction was occurring. Therefore, this approach was discontinued.

A fourth attempt, an acid-catalyzed heterogeneous reaction, was somewhat successful. This procedure was also patterned after a published procedure.[10] In this reaction, a mixture of isophthalamide, ethyl bromooxaloacetate and a catalytic amount

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of concentrated sulfuric acid were refluxed in benzene for several days. Although the isophthalamide was not soluble in benzene, a small amount of the desired monomer was isolated, along with di-, mono-alkylated isophthalamide, and a mono-oxazole functionalized compound. This reaction further illustrated that the desired monomer is a stable compound and would be best prepared from an intermediate such as Compound 16. Thus, Compound 16 became a synthetic target in other attempts as a precursor to the desired monomer.

Another route to the monomer via an indirect alkylation of isophthalamide is shown in Figure 13. Instead of alkylating isophthalamide, N,N'-bis-benzyl isophthalamide (Compound 17) was prepared from isophthaloyl chloride and benzylamine in a straightforward reaction. Unlike isophthalamide, N,N'-bis-benzyl isophthalamide was found to be soluble in numerous organic solvents. In the next step, we attempted to silylate the amide by refluxing it in excess hexamethyldisilazane. Our motive was to activate the amide for subsequent alkylation with ethyl bromooxaloacetate. Unfortunately, Compound 17 was not soluble in hexamethyldisilazane, a higher boiling silylating reagent than the trimethylsilyl chloride used previously. The reaction mixture remained heterogeneous, after about one week of reflux, with no other indicators that a reaction occurred. There are alternate procedures that are still available for alkylating Compound 17, should there be a desire for future attempts. One of these
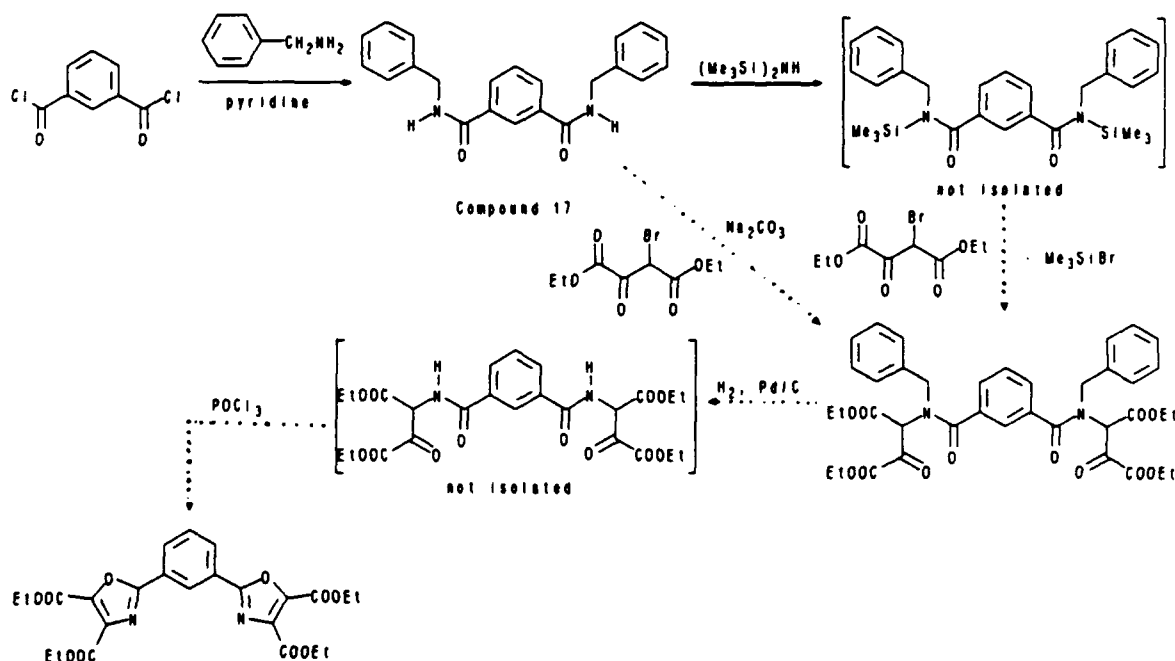

Figure 13. Alternate route to monomer for RO-membrane polymer.

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alternate procedures, using a stronger base to treat Compound 17 before reacting with an alkylating agent, is also shown in Figure 13.

d. Starting from isophthaloyl chloride via acylated enolate

The route shown in Figure 14 was devised based on the known susceptibility of enolates and acylated eneamines to halogenation with either chlorine or bromine.
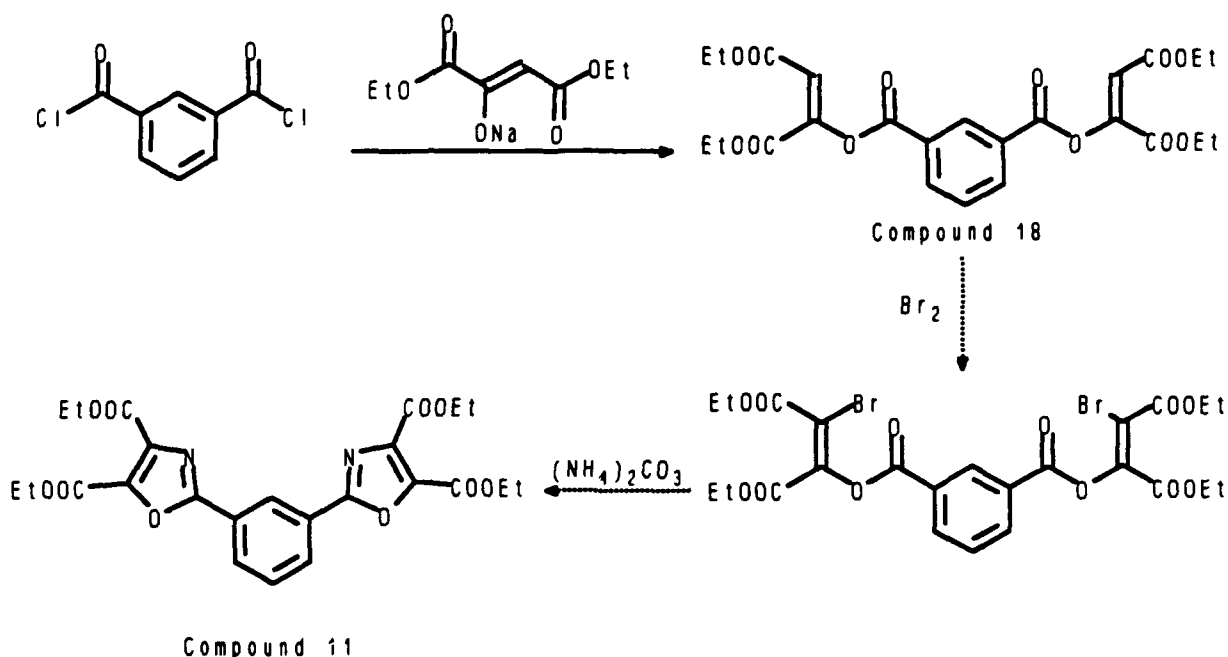

Figure 14. Alternate route to polymer for RO-membrane starting from dimaleimide.

This led us to establish Compound 18 as a potentially viable intermediate towards the highly sought monomer. Because of the high reactivity of isophthaloyl chloride, the acylation of the enolate anion of sodium diethyl oxaloacetate was expected to be straightforward, but this was not the case. None of the expected product (Compound 18) was isolated and neither was any monoesterified isophthalate, which could have indicated that the reaction had potential. Instead, an unstable compound was apparently formed, as evidenced by a series of color changes during its attempted isolation.

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e.   Starting from isophthalate salts via acylated α-hydroxy-ketone intermediate

Based on numerous reports for obtaining oxazoles via ring-closure of acylated α-hydroxy-ketones, we established the structure identified as Compound 19 in Figure 15 as a potential precursor towards the required monomer and devised the synthetic routes shown in the Figure. All of the routes in this approach began with a salt of isophthalic acid, which was prepared by titrating isophthalic acid with the appropriate base. The subsequent step of alkylating the isophthalate salt with ethyl bromooxaloacetate (Compound 15) was expected to afford the acylated α-hydroxy-ketone intermediate (Compound 19). The first attempt to this approach was the
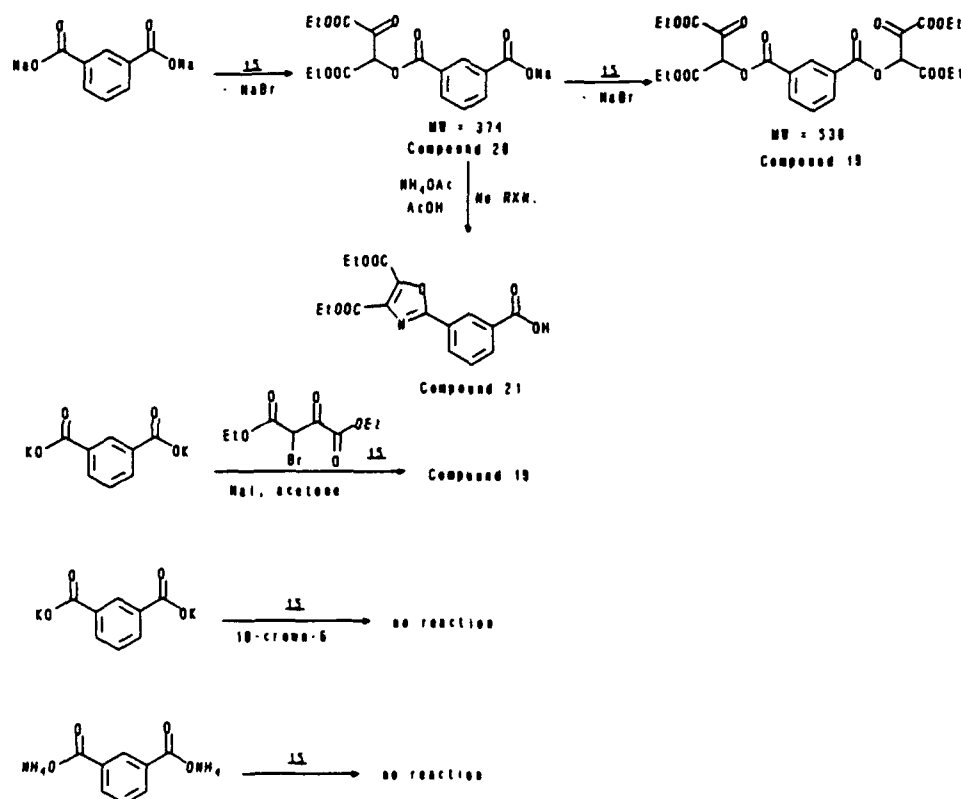

Figure 15. Side product formation in reaction with ethyl bromooxaloacetate.

reaction sodium isophthalate with ethyl bromooxaloacetate (Compound 15). The reaction was performed using a stoichiometric ratio of 1 part sodium isophthalate to 2 parts of Compound 15 with ethanol as solvent. In this first attempt, only an intermediate identified as Compound 20 in Figure 15 was isolated. In the subsequent reaction, acetone was used as solvent and we used potassium isophthalate instead of the sodium isophthalate because it had better solubility than the sodium salt. We also

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used a large excess of the ethyl bromooxaloacetate and a catalytic amount of sodium iodide. This modification led to the formation of a mixture of products that had an unusual mass spectrum. The MS data did not show the 538 molecular-weight ion for the desired compound. Instead, a molecular-weight ion corresponding to the complex of the MW 538 with sodium cation was observed at MW 561. Furthermore, additional molecular weight cations at 567, 583, and 599 indicate a loss of proton from the MW 561 followed by complexation of either, lithium, sodium, or potassium, respectively. The lithium complexation results from the use of lithium chloride in the MS technique and the sodium and potassium were originally present in the reaction mixture for the complexation. This multi-cation complexation is a phenomenon that is rarely encountered in mass spectrometry.

In addition to the complexes of the desired product, a MW of 375 was also observed, which is the cation of a mono-substituted isophthalate with sodium as the counterion for the unsubstituted carboxylic acid. The MW 375 cation, when deprotonated, could also complex with sodium and potassium to account for the additional MW's at 397 and 413, respectively.

Further attempts to optimize this reaction did not bear fruit. We investigated the feasibility of the subsequent ring-closure reaction using the product mixture that contained both Compounds 19 and 20 as the model compounds. This would have established the viability of approaching the monomer through α-hydroxy-ketone intermediates. However, the ring closure reaction, which involved refluxing the compound mixture in acetic acid in the presence of ammonium acetate, did not yield even traces of either Compound 21 (shown in Figure 15) or Compound 11 (shown in Figure 14). This ultimately led us to abandon the approach towards the monomer via α-hydroxy-ketone intermediates.

Before abandoning this approach, we attempted the reaction of potassium isophthalate with ethyl bromooxaloacetate in the presence of a catalytic amount of 18-crown-6 (not to be confused with the aza-crown-ether). Tetrahydrofuran, a polar aprotic low boiling liquid, was the solvent in the reaction. The 18-crown-6 was expected to act as a phase transfer catalyst by complexing with potassium to help solubilize the isophthalate salt. In this method, the reaction mixture was refluxed and remained heterogeneous from start to finish. The TLC indicated formation of a new chemical species, and the mixture changed color during the course of the reaction. After filtering the suspected product from the reaction mixture, it was analyzed by MS. None of the molecular weights in the spectrum could be attributed to an expected product or intermediate. However, there was an unexpected side reaction as a result of the presence of diethyl oxaloacetate as a contaminant of the ethyl bromooxaloace-tate. The side reaction led to the formation of a dimerized diethyl oxaloacetate as shown in Figure 16. This indicated that the α-hydrogens in the ethyl oxaloacetate were acidic and easily deprotonated by the carboxylate anion. As a result, a new base formed that acted as the nucleophile and displaced the bromide in ethyl bromo-

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oxaloacetate. This procedure could have worked if the alkylating agent was made purer.
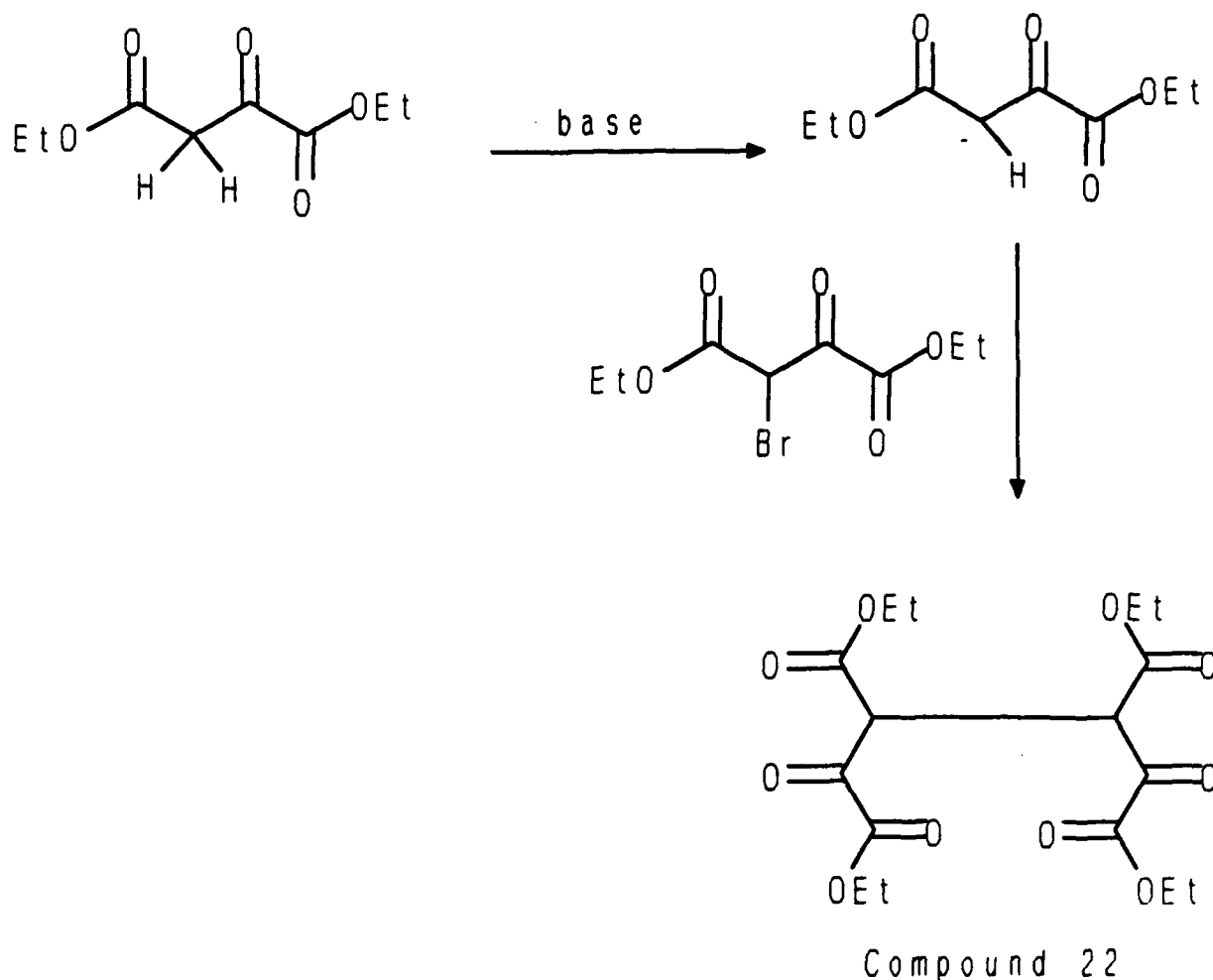

Figure 16. Formation of bis-diethyloxaloacetate in synthesis of ethyl bromooxalo-acetate.

Another isophthalate salt that was reacted with ethyl bromooxaloacetate was ammonium isophthalate, which was prepared by simply neutralizing isophthalic acid with concentrated ammonium hydroxide. The rationale in using ammonium isophtha-late, a precursor of isophthalamide, is that it may be a one-step route to the desired monomer. However, this reaction also led to the formation of a bis-diethyl oxalo-acetate.

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<u>Starting from the sodium salt of diethyl oxaloacetate</u>

Based on the known nitrosation reaction of 6-keto esters to yield α-oximino-6-keto compounds and the known reactions of this class of compounds for the preparation of oxazoles or oxazole precursors, we established the synthetic route shown in Figure 17. For this route, diethyl α-oximino-oxaloacetate (Compound 23) was the key intermediate to be synthesized. In the first step, we adapted a procedure from the literature that was used to convert ethyl acetoacetate into ethyl oximino-acetoacetate.[11] The adapted procedure called for dissolving the keto-ester in glacial
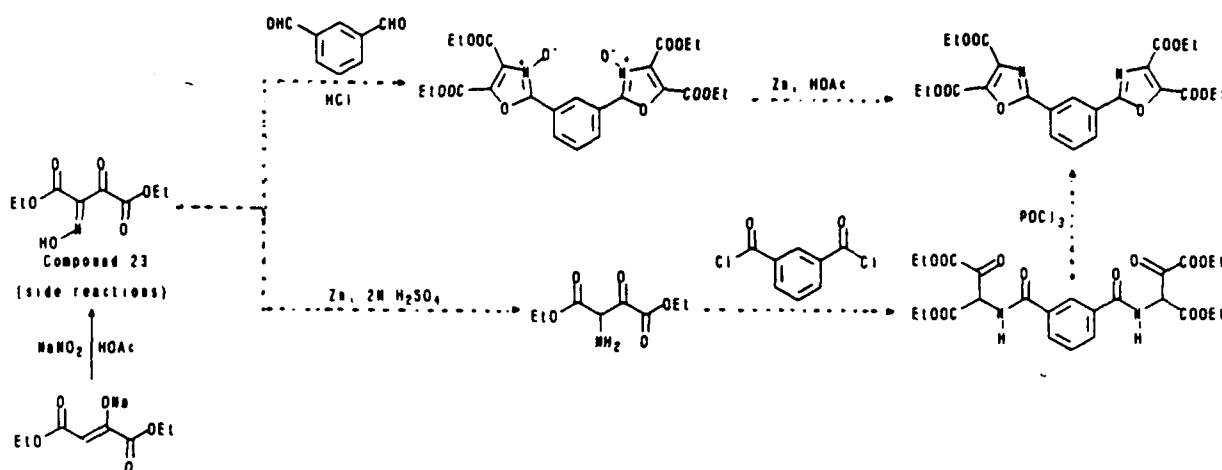

Figure 17. Alternate route to monomer for RO-membrane polymer via α-oximino-β-keto intermediate.

acetic acid and adding sodium nitrite to the mixture at room temperature. Diethyl oxaloacetate is a 6-keto ester that would have been preferred as the starting material, but it was not readily available. Its sodium salt was available and was thought to generate the required ethyl oxaloacetate in situ when placed in the glacial acetic acid. Unfortunately, the attempted nitrosation sodium diethyl oxaloacetate did not yield the oximino derivative (Compound 23, Figure17). The main problem we encountered in this step was the lack of solubility and therefore reactivity of sodium diethyl oxaloacetate in acetic acid. Because of this result and more encouraging results in other approaches, this route was not pursued any further.

g. <u>Starting from ethyl nitroacetate</u>

As part of our efforts on the preparation of the required monomer via an isophthalamide derivative, ethyl nitroacetate (Compound 24) was envisioned to be a

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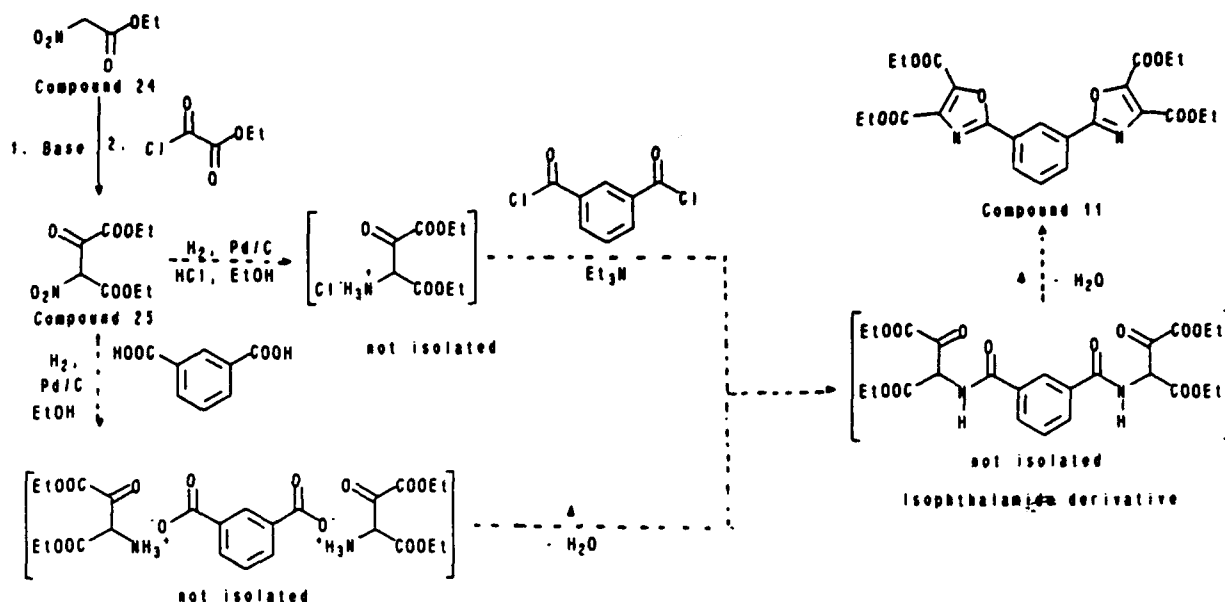viable starting material using the route shown in Figure 18. This compound is a

Figure 18. Alternate route to monomer for RO-membrane polymer via α-nitro-β-ketone.

versatile synthon in heterocyclic chemistry for constructing fused ring systems.[12] It is commercially available, but it can be readily prepared from nitromethane using reliable procedures.[13] We attempted the first reaction twice in an effort to prepare ethyl nitrooxaloacetate (Compound 25). In the process, we varied only the base needed to deprotonate the α-carbon of ethyl nitroacetate. In one of the two attempts, there was no reaction when 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was used as base in the reaction of ethyl oxalylchloride with ethyl nitroacetate. Initially, we thought a reaction had occurred based on observations of exothermicity, color change, and precipitate formation. However, upon work-up and isolation of an oily product, its analysis by NMR spectroscopy indicated that it was not product nor side products of any anticipated potential side reactions. In the other attempt, there were only traces of product formation when sodium hydride was used as base. After these two unsuccessful attempts, we abandoned this approach.

h.   Starting of 1,3-phenylenedimaleimide

Shown in Figure 19 is a route to the polymer that does not use the phenylene-bis-oxazole functionalized monomer we have been discussing in previous sections. Currently this route appears to have the most promise. We have attempted this route twice. In our first attempt, we used the 1,3-phenylenedimaleimide as is from the commercial source. This led to the isolation of a crude Compound 26, which was difficult to purify, although the NMR spectrum of the crude product mixture indicated a
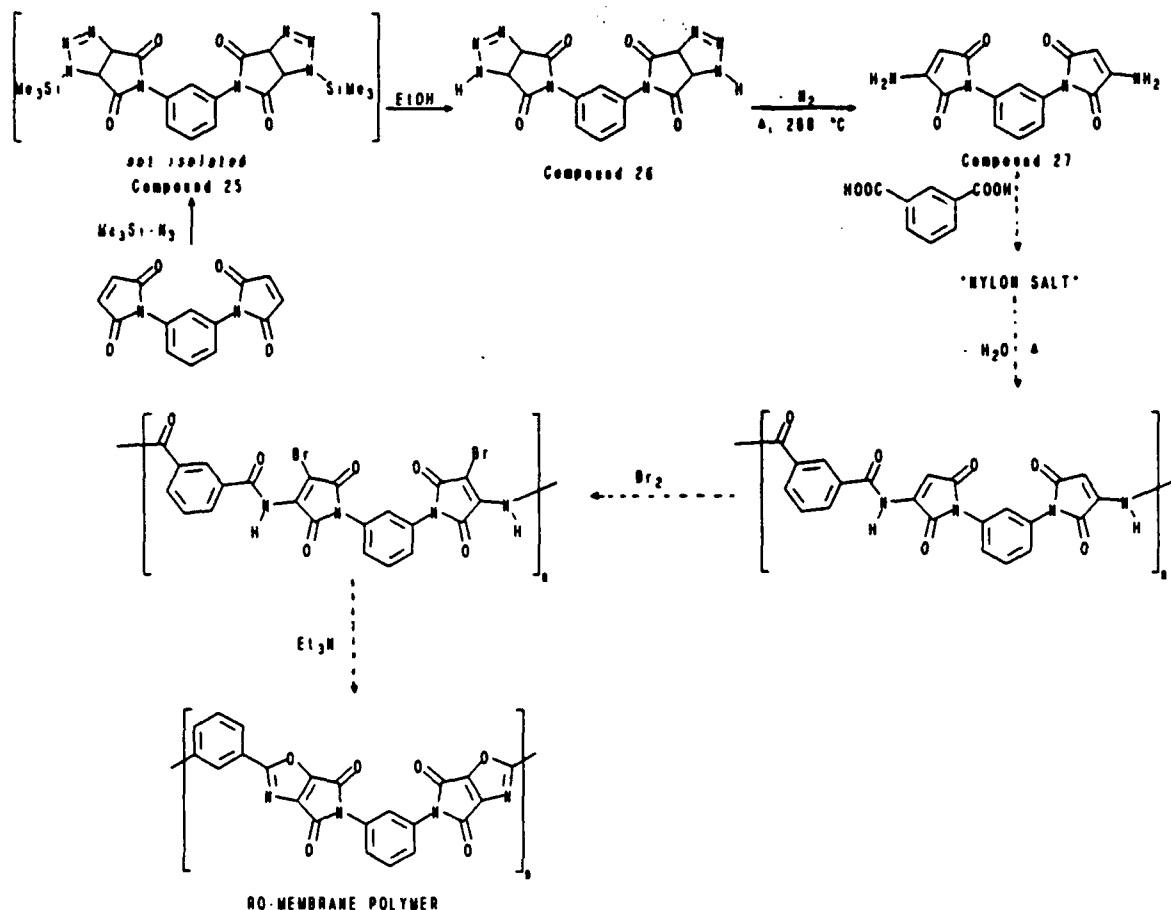
Figure 19. Alternate route to monomer for RO-membrane polymer via α-oximino-β-keto intermediate.

very high content of the desired product. In the second attempt, we purified 1,3-phenylenedimaleimide by recrystallization from ethanol before carrying out the synthetic route. This made the purification of Compound 26 easier. The first step of the route was adapted from a literature procedure and was found to be straightforward.[14] In this step, the 1,3-phenylenedimaleimide was refluxed overnight with two equivalents of trimethylsilylazide in xylene. The reaction mixture was then worked up by distilling the mixture to dryness leaving Compound 26 as residue. In the second step, ethanol was then added to the residue and the new heterogeneous mixture was refluxed overnight to cleave off the trimethylsilyl groups of Compound 25. Filtration of the solids afforded the desired product (Compound 26) in nearly quantitative yield.

The next step was the thermal decomposition of the triazole moieties to transform them into amino groups. This procedure and the first two steps were adapted from the same reference. In the third step, Compound 26 was mixed with diphenyl ether and the heterogenous mixture was heated to 200 °C until no more

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nitrogen gas was evolved. Isolation of the product by filtration, washing with diethyl ether, and drying afforded the diamino monomer (Compound 27) as a yellowish brown powder in quantitative yield. Thus, the overall yield in the synthesis of the monomer is practical. Interestingly, the monomer was recrystallizable from water, which could be an indication that polymers derived from this monomer might have good moisture permeability.

The polymerization and polymer modification steps, also shown in Figure 19, have not been performed and should be considered for inclusion with any future work carried out in developing the polymer. The polymerization would be straightforward because it is based on known technology for preparing polyamides. However, the polymer modification steps could potentially run into difficulties if the polymer is insoluble in the solvents that are typically used for the bromination. A procedure for the bromination that could be adapted calls for the use of chloroform or dichloromethane as solvent. It is highly unlikely that the polymer will be soluble in such solvents.[15] However, the polymer will probably be soluble in polar aprotic solvents such as dimethyl formamide, N-methyl pyrrolidinone, or dimethylsulfoxide, which can also be used in such reactions instead of the halogenated solvents, although there may be decreases in the degree of an otherwise quantitative conversion. The subsequent step, which is the ring-closure, should be straightforward to obtain the polymer that would be used for fabrication of prototype RO-membrane.

III. CONCLUSIONS AND RECOMMENDATIONS

Although the polymer for the F/C has not been optimized in terms of composition as a function of performance properties, the result of the preliminary evaluation of the prototype polymer supports the premise by which the polymer was designed; that is, metal complexing groups that are covalently attached to known F/C polymers will be more efficient in clarifying turbid waters by introducing additional pathways for floc formation. Because the metal complexing group we used was specific for binding sodium or potassium ions, it may not necessarily have the ability to complex a broad spectrum of metal ions that could be present in turbid waters or on the surfaces of colloidal particles. Thus, in future F/C polymer development efforts, an appropriate target polymer would be similar except that the side chains would be short segments of polyethyleneglycol.

In the development of the RO-membrane polymer, a three-step synthetic route to a monomer has been developed that appears to be nearly quantitative in overall yield. Furthermore, the monomer exhibited physical properties, such as high temperature stability and water-solubility, which could potentially lead to a polymer with high thermal stability and high water-permeability. Thus, the polymer structure

designed for the RO-membrane should continue to be a highly desirable objective. We believe the difficulties are behind us in the preparation of monomers for the RO-membrane. The next phase in continuation of this project should be polymer synthesis and RO-membrane development and evaluation.

IV. ACKNOWLEDGEMENTS

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